Studies on Extraction and Determination of Metal Salts with Methyl Isobutyl Ketone. IX. : Photometric Determination of Iron and Cobalt in Electric Heating Alloys

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Photometric Determination of Iron and Cobalt in Electric Heating Alloys*

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(Received February 27, 1964)

Synopsis

0.5~0.001 per cent of cobalt in iron-chromium electric heating alloy was easily determined by photometric method. In the case of nickel-chromium electric heating alloy, simultaneous determination was possible when the content ratio of iron to cobalt was less than one half and the total amount of cobalt in the sample was over 0.01 per cent.

I. Introduction

There are numerous methods for the determination of microquantity of cobalt in iron and steel, and the photometry of the nitroso-R salt is the method usually used.[1-8] This method is comparatively easy and rapid, without requiring separation of iron, but is not adapted for samples containing a large amount of nickel. A method using extraction with 2-nitroso-1-naphthol and ethyl acetate-butyl acetate,[9] or with the same reagent and benzene extraction[10] is said to be sensitive for the determination of microquantity of cobalt in iron and steel. In

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the previous series, the photometric determination of such cobalt as a thiocyanate[11] and the concurrent determination of cobalt and iron in metallic nickel have been reported[12]. The application of these methods of the determination to iron-chromium and nickel-chromium electric heating alloys gave satisfactory results. This method was adopted as the Japanese Industrial Standard (JIS) method.

II. Determination of cobalt in iron-chromium electric heating alloy

The determination of cobalt in iron-chromium electric heating alloy was carried out by the method already reported[11] for the determination of cobalt in iron and steel.

1. Determination of cobalt

As previously reported the absorption maximum of cobalt thiocyanate in the visible region lies at 625~635mμ, and 630mμ is convenient for the measurement. Optimal conditions for the determination of cobalt are to make hydrochloric acid concentration below 1N and ammonium thiocyanate concentration above 3M, and therefore, hydrochloric acid concentration of 0.5N and ammonium thiocyanate concentration of 4M were used. The determination of cobalt in iron-chromium sample was made after removal of majority of iron and chromium by extraction with methyl isobutyl ketone from hydrochloric acid solution, but preoviously stated,[11] a reduction agent, preferably stannous chloride, was necessary to remove the effect of a small amount of residual iron. In accordance with these facts, stannous chloride was used and this was found to be convenient for the reduction of a small amount of residual chromic acid. As for the effect of other co-existing elements, as already stated, titanium, niobium, tungsten, and molybdenum are extracted as their thiocyanate but tungsten and molybdenum are not usually contained in this kind of samples. Even if present as impurities, they would not affect the determination of cobalt under these conditions. Titanium is likely to be present and it must be removed. Titanium can be separated by basification with ammonia, as used in the cases of iron and steel samples.[11] This procedure will remove niobium also if present.

2. Analysis of iron-chromium electric heating alloy

(1) Reagents and apparatus

Reagent:

Standard cobalt solution: pure metallic cobalt was weighed accurately, dissolved in a small amount of nitric acid, and diluted with water to a definite volume to make a solution containing 1 mg/ml. This stock solution was diluted

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with water on use.

Ammonium thiocyanate solution: 8M aqueous solution.

Hydrochloric acid: 10N.

Nitric acid. perchloric acid, stannous chloride, methyl isobutyl ketone: first grade, chemical

Apparatus:

Hitachi photoelectric spectrophotometer model EPU-2A

(2) Calibration curve

Various amounts of standard cobalt solution, with $0 \sim 300\,\mu g$ of cobalt, were diluted with water to about $3 \sim 4$ ml, 5 ml of 10N hydrochloric acid and 5 ml of 8M ammonium thiocyanate were added, and diluted to 10 ml with water. 2 g of stannous chloride was added, the whole was shaken to effect dissolution, 10 ml of methyl isobutyl ketone was added from a burette, and the whole was shaken vigorously for about 30 seconds. The organic layer was separated and the absorbance of this extract solution was measured at 630 mμ, from which a relationship between the amount of cobalt and the absorbance was plotted.

(3) Analytical procedure

Sample is weighed for $0.01 \sim 2$ g, dissolved in a mixture of $10 \sim 20$ ml of hydrochloric acid solution (1: 1) and $3 \sim 10$ ml of nitric acid, $3 \sim 10$ ml of perchloric acid is added, and the mixture is heated until white fumes evolve. The mixture is further heated to oxidize chromium thoroughly, but there is no necessity for the evaporation until dryness. To this mixture, $0.5 \sim 1$ ml of nitric acid is added and the mixture is transferred to a separatory funnel with the aid of $10 \sim 30$ ml of 6N hydrochloric acid. Methyl isobutyl ketone of the same amount as the acid used is added and the mixture is shaken rapidly for 30 seconds. The lower acid layer is transferred to another separatory funnel and again extracted with the same volume of methyl isobutyl ketone. The lower acid solution is transferred to a beaker and evaporated to less than 10 ml when the volume is more than 10 ml. This solution is diluted with $10 \sim 30$ ml of water and basified with excess ammonia water.

This solution is filtered and the filter is washed several times with water. The combined filtrate with washings is concentrated to about 5 ml, 0.5 ml of 10N hydrochloric acid is added, and transferred to a separatory funnel. The beaker is washed out with 5 ml of 8M ammonium thiocyanate, the washings are combined with the solution in the separatory funnel, and 2 g of solid stannous chloride is added. After complete dissolution, 10 ml of methyl isobutyl ketone is added, and subsequent extraction and measurement of the absorbance at 630 mμ are carried out as in the case of the preparation of the calibration curve.

Blank test is carried out with the same reagents and in the same way, and correction is made in the absorbance. The amount of cobalt in the sample is calculated from the calibration curve.

(5) Aanlytical result

The results obtained by this method with synthetic samples are listed in Table 1, which indicates good agreement. A comparatively large value of blank tests is due to the presence of cobalt in the electrolytic iron used. Values obtained from the samples with addition of cobalt were subtracted as the blank values. From the satisfactory results obtained with synthetic samples, the method was applied to actual samples and the result thereby obtained is listed in Table 2.

Table 1. Analytical results of synthetic samples.

Fe, Cr and other metals taken (g)	Co added (μg)	Absorbance		Co found (μg)
		Blank	Co complex extract against blank	
Fe 0.200 Cr 0.090	55 〃	0.074 〃	0.246 0.244	54 55
〃 〃	110 〃	0.074 〃	0.490 0.488	110 109
Fe 0.200 Cr 0.090 Ti 0.0017	55 〃	0.076 〃	0.243 0.241	54 54
〃 〃	110 〃	0.076 〃	0.487 0.482	109 108

Table 2. Analytical results of iron-chromium electric heating alloy samples.

Sample	Sample taken (g)	Aliquot	Absorbance against blank	Co (%)	Nitroso-R salt method Co (%)
Sample 1	1.0000 〃 〃	1/10 〃 〃	0.084 0.086 0.082	0.036 0.038 0.035	0.035
Sample 2	1.0000 〃 〃	1/10 〃 〃	0.076 0.086 0.084	0.034 0.038 0.036	0.030
Sample 3	1.0000 〃 〃	1/10 〃 〃	0.039 0.042 0.042	0.017 0.018 0.018	0.017
Sample 4	1.0019 〃 〃	1/10 〃 〃	0.055 0.062 0.062	0.024 0.027 0.027	0.023
Sample 5	0.1990 〃 〃	1/10 〃 〃	0.338 0.340 0.343	0.75 0.76 0.76	
Sample 6	0.2021 〃 〃	1/10 〃 〃	0.320 0.330 0.330	0.70 0.72 0.72	

III. Determinations of cobalt and iron in nickel-chromium electric heating alloys

Determinations of cobalt and iron in nickel-chromium electric heating alloys were carried out according to the photometric determinations of microquantities of cobalt and iron in metallic nickel already reported.[12]

1. Determinations of cobalt and iron

Conditions for the determination of cobalt were the same as those in iron-chromium samples. As already reported for the determination of iron,[12] iron colored red as ferric thiocyanate and was extracted with an organic solvent. It was extracted and determined under the same condition as in the case of cobalt.

As shown in Fig. 1, the absorption maximum of ferric thiocyanate extracted in methyl isobutyl ketone solution is around 510 mμ and there is a slight absorption at 630 mμ, at which cobalt thiocyanate showed absorption maximum. Therefore, 530 mμ, at which there is almost no absorption of cobalt, was used for the measurement of iron absorption.

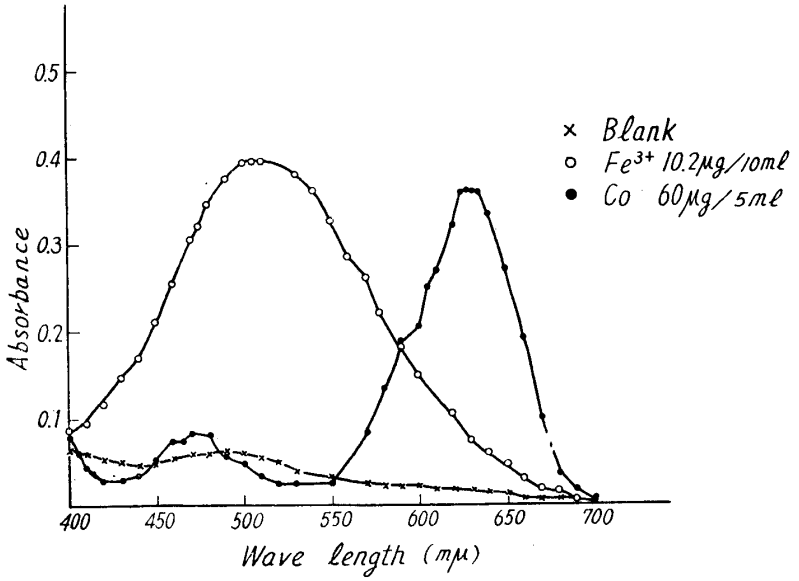

Fig. 1. Absorption curve of Co and Fe thiocyanate.

As for the stability of ferric thiocyanate in methyl isobutyl ketone solution, it was more stable than in acid solution, the absorbance did not decrease at all for about one hour, and the discoloration was very slight.[12] Consequently, ferric thiocyanate could be used for the determination of iron, being the same as the case for cobalt.

Nickel did not affect the extractions of cobalt and iron, but chromic ion was extracted as thiocyanate to a slight degree. Therefore, when there is a large quantity of chromic ion, as the case of taking large amount of the sample, it becomes

necessary to remove majority of chromium.

2. Analysis of nickel-chromium electric heating alloy

(1) Reagents and apparatus

Reagents: standard cobalt solution, ammonium thiocyante solution, hydrochloric, nitric, and perchloric acids, stannous chloride, and methyl isobutyl ketone were all the same as those in the case of iron-chromium electric heating alloy.

Standard iron solution: electrolytic iron was weighed accurately, dissolved in nitric acid and diluted with water to make a solution of 0.1 mg/ml as ferric ion. This stock solution was diluted with water on use.

Apparatus: same as for iron-chromium samples.

(2) Calibration curves

(a) Calibration curve for iron

Various amounts of standard iron solution, with $0 \sim 25$ μg of iron, were diluted to about $3 \sim 4$ ml with water, 5 ml of 10N hydrochloric acid and 5 ml of 8 M ammonium thiocyanate were added, and diluted to 10 ml with water. To this solution, 10 ml of methyl isobutyl ketone was added from a burette, and the mixture was shaken vigorously for about 30 seconds. The methyl isobutyl ketone layer was separated and its absorbance was measured at 520 and 630 mμ to prepare the calibration curves. The curve for 520 mμ was used for the determination of iron and that for 630 mμ for correcting the absorption of cobalt.

(b) Calibration curve for cobalt (without addition of stannous chloride)

The curve was prepared in the entirely same way as in the case of cobalt in iron-chromium electric heating alloy.

(3) Analytical procedure

(a) Simultaneous determination of cobalt and iron (with more than 0.01 per cent of cobalt, with less than one half of iron amount)

A solution of $0.1 \sim 1$ g of the sample dissolved in 20 ml of aqua regia is diluted with water, transferred to a 100 ml measuring flask, and brought to 100 ml with water. A 10 ml portion of this solution is transferred to a beaker by a pipette, $5 \sim 10$ ml of perchloric acid is added, and the solution is heated until thick white fumes evolve. Hydrochloric acid is added little by little and the mixture is heated to evaporate majority of chromium. The mixture is heated further until it becomes almost dry, 0.5 ml of 10N hydrochloric acid is added to the residue and transferred to a separatory funnel with the aid of 4.5 ml of water. To this solution, 5 ml of 8 M ammonium thiocyanate is added and shaken vigorously with 10 ml of methyl isobutyl ketone for about 30 seconds. The upper ketone layer is separated and its absorbance is measured at 630 and 520 mμ. The absorbance of iron can be measured at 520 mμ without the effect of cobalt and the quantity of iron is calculated from the calibration curve for iron at 530 mμ. The absorbance of

iron of this quantity at 630 mμ is subtracted from that measured at 630 mμ, and the difference is the absorbance for cobalt. The quantity of cobalt is calculated from the calibration curve for cobalt (without addition of stannous chloride). There is no need for the procedure to eliminate chromium when the amount of sample taken is less than 0.3 g.

(b) Determination of cobalt alone

With cobalt above 0.01 per cent: A solution of 0.1~1 g of the sample dissolved in 20 ml of aqua regia is diluted with water, transferred to a 100 ml measuring flask, and brought to 100 ml with water. A 10 ml portion of this solution is transferred to a beaker, 5~10 ml of perchloric acid is added, and the mixture heated until thick white fumes evolve. Hydrochloric acid added little by little and the solution is heated to vaporize majority of chromium. The residue is dissolved in 0.5 ml of 10N hydrochloric acid and the solution is transferred to a separatory funnel with the aid of 4.5 ml of water. To this solution, 5 ml of 8 M ammonium thiocyanate is added, followed by 2 g of solid stannous chloride, and the mixture is shaken to dissolve the crystals. The mixture is shaken with 10 ml of methyl isobutyl ketone, the methyl isobutyl ketone layer is separated, and its absorbance is measured at 630 mμ. The quantity of cobalt is calculated from the calibration curve (with addition of stannous chloride). There is no need to vaporize chromium when the amount of sample taken is less than 0.3 g.

With less than 0.01 per cent of cobalt: A solution of 0.3~1 g of the sample dissolved in 10~30 ml of aqua regia is evaporated to dryness, the residue is dissolved in 3 ml of 10N hydrochloric acid, and the solution is transferred to a separatory funnel with the aid of 22 ml of water. The whole volume is brought to 50 ml with 25 ml of 8 M ammonium thiocyanate and the solution is shaken with 50 ml of methyl isobutyl ketone for about 30 seconds. The lower aqueous solution is discarded, methyl isobutyl ketone layer is transferred to a small beaker, and the separatory funnel washed out with 1~2 ml of methyl isobutyl ketone. The combined ketone solution is evaporated, 2~3 ml of each of nitric and perchloric acid added, and the solution is heated to decompose organic matter. The residue obtained after the evaporation of the solution dissolved in 0.5 ml of 10N hydrochloric acid to effect dissolution and transferred to a separatory funnel with the aid of 4.5 ml of water.

To the solution in the separatory funnel, 5 ml of 8M ammonium thiocyanate and 2 g of solid stannous chloride are added consecutively and shaken to effect dissolution. This solution is shaken with 10 ml of methyl isobutyl ketone for about 30 seconds and the absorbance of the ketone layer is measured at 630mμ.

When the amount of iron is comparatively large and the solution turns deep red at the first extraction, the following procedure is adapted. The initial extract solution is evaporated to dryness, the residue is transferred to a separatory funnel with the aid of 10 ml of 8N hydrochloric acid, 10 ml of methyl isobutyl ketone is added, and the whole is shaken for about 30 seconds. The lower layer is transferred

to a beaker, evaporated, and 1～2 ml of each nitric and perchloric acid are added. This is heated to decompose organic matter and further to dryness. The residue is treated as in the foregoing to determine cobalt by extraction.

Table 3. Analytical results of synthetic samples.

Ni, Cr taken (g)	Fe added (μg)	Co added (μg)	Absorbance 520mμ	Absorbance 630mμ	Fe found (μg)	Co found (μg)
Ni 0.080 Cr 0.020	7.0 〃	129.5 〃	0.251 0.249	0.442 〃	7.1 〃	131.0 〃
〃	15,0 〃	64.8 〃	0.532 0.510	0.262 0.264	15.3 15.2	62.0 62.5
〃	20.0 〃	104.3 〃	0.719 0.700	0.709 0.710	20.7 20.2	195.2 197.0

Table 4. Analytical results of nickel-chromium electric heating alloy samples (Co solution added).

Sample	Sample taken (g)	Aliquot	Co added (μg)	Co added (%)	Absorbance 520mμ	Absorbance 630mμ	Fe found (%)	Co found (%)
Sample 1 Co 0.022% Fe 0.11 %	0.1225 〃 〃	1/10 〃 〃	129.5 〃 〃	1.057 〃 〃	0.449 0.439 0.483	0.474 0.466 0.474	0.105 0.103 0.113	1.078 1.061 1.072
〃	0.1125 〃 〃	1/10 〃 〃	51.8 〃 〃	0.423 〃 〃	0.443 0.433 0.450	0.223 0.212 0.216	0.104 0.101 0.105	0.429 0.408 0.416

Table 5. Analytical results of nickel-chromium electric heating alloy samples.

Sample	Sample taken (g)	Aliquot	Absorbance against blank	Co (%)	Remark
Sample 1	3.0608	1/10	0.155	0.022	Cr was volatilized
			0.155	0.022	
	2.8903		0.145	0.022	
			0.146	0.022	
Sample 2	0.2000	1/10	0.245	0.54	Cr was not volatilized
			0.245	0.54	
	0.2500		0.305	0.54	
			0.302	0.53	

(4) Analytical results

Result of simultaneous determination of cobalt and iron with synthetic samples is given in Table 3, which shows a satisfactory agreement. Iron and cobalt added to nickel-chromium sample were those obtained by extraction and isolation by a similar method. Samples with suitable ratio of cobalt to iron content were not available for simultaneous determination of cobalt and iron, and samples were

added with a suitable quantity of cobalt. The amount of samples taken became small according to the quantity of iron present in the sample and vaporization of chromium was not carried out. These results are given in Table 4, which shows that the determination gives the result agreeing well with the content of iron in the sample, and that the amount of cobalt agrees with the amount of cobalt added. Results of the determination of cobalt alone are given in Table 5 and satisfactory results were obtained also in this case. The method using the nitroso-R salt tended to show lower values in the presence of a large amount of nickel.